

Chalcocite as a potential material for supercapacitors

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Abstract

Natural copper minerals covellite and chalcocite have been investigated using different electrochemical methods (galvanostatic, potentiostatic, cyclic voltammetry and electrochemical impedance spectroscopy) from the point of view of their capacitive behavior. The highest value of capacitance (about 200 F cm^{-2}) was obtained on chalcocite in electrolyte containing $1 \text{ M H}_2\text{SO}_4$ and 0.5 M CuSO_4 , but with unacceptable high leakage current. Optimal system from the both criteria is chalcocite in $1 \text{ M H}_2\text{SO}_4$ and 0.1 M CuSO_4 , where the capacitance of about 110 F cm^{-2} has been obtained. Copper sheet served as a counter electrode. Electrochemical impedance spectroscopy method had to be adopted for the systems containing high capacitances. The existence of reaction product on the surface of investigated minerals has been established by optical and electron microscopy.

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1. Introduction

Supercapacitors fulfill a very wide area between accumulator batteries and conventional capacitors taking into account specific energy and power [1–5]. Batteries and fuel cells are typical devices of small specific power, while conventional capacitors can have specific power higher than 1 MW dm^{-3} , but at a very low specific energy. Electrochemical capacitors improve batteries' characteristics considering specific power or improve capacitors characteristics considering specific energy in combination with them. In relation to other capacitor types, supercapacitors offer much higher capacitance and specific energies, which make those devices adequate for purposes requiring great specific energy and great specific power combination or long lifetime denoted by charging and discharging number of cycles [1,3,4]. In other words, supercapacitors have retained classical capacitors positive property to achieve almost unlimited charging and discharging number of cycles.

Literature offers data on two basic kinds of supercapacitors with different ways for energy storing [1,5–7]:

- (a) double layer capacitors and
- (b) pseudocapacitors.

Capacitance of the first kind is electrostatic by its nature, taking into account that distance between quasi electrodes is extremely short, and electrode material has highly developed surface. Typical examples are Faraday inactive carbon powders including both assumptions. The name electrochemical double layer (EDL) capacitor describes the elementary principle of energy storing at those devices. Principally, energy storing at double layer capacitor is a result of electrical charge separation at the interface between electrode as electronic conductor and electrolyte as ionic conductor. Capacitance created at that interface is the double layer capacitance. Owing to the large specific area, carbon is one of the best examples of materials for double layer capacitors.

A typical representative of EDL capacitors is the carbon material-based system [8–10]. Such systems reach specific capacitance over 200 F g^{-1} depending on the way electrode material is processed and the type of electrolytes used [3,11–16].

Pseudocapacitance arises in some electrosorption processes and in redox reactions at some electrode surfaces. Investigation of materials by cyclic voltammetry method showed extremely capacitance behavior that cannot be explained only by double layer capacitance [6,17]. The latest researches in this field

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are focused to the development of supercapacitors based at fast reversible Faraday reactions. Typical representatives of the redox supercapacitors are RuO_2 , Co_3O_4 , NiO_2 and IrO_2 in acid water solutions. Specific capacitances realized at those supercapacitors are from 50 to 200 F g^{-1} , specific energy from 25 to 40 kJ kg^{-1} and specific power $4\text{--}17 \text{ kW kg}^{-1}$. Extraordinary, authors in literature [18] report that they realized pseudocapacitance of even 750 F g^{-1} at ruthenium dioxide synthesized at relatively low temperature.

Pseudocapacitors have rather greater values of specific energy comparing to carbon double layer capacitors. Besides, electrical conductivity of metal oxide (RuO_2) is extremely higher than at carbons and all together lead to greater specific power or, in other words, to less RC (resistance–capacitance) value of time constant. The pseudocapacitors advantages are decreased by their high price compared to carbon. However, advantages realized with carbon materials can be combined with advantages achieved with transient metals oxides, so it led to the new class of electrochemical capacitors. Development of combined double layer Faraday pseudocapacitors as a result may have the use of the advantages of metal oxide Faraday capacitance and carbon material double layer capacitance [19,20].

The development of nanotechnology referring to electrode material enables the insight into new perspectives, and thus, the improvement of supercapacitors' features [12,21–27].

Many results of electrochemical researches on copper sulfides can be found in literature [28–30], but none referring to the materials as potential electrode material for supercapacitors.

Investigations of behavior of copper sulfide minerals during their anodic polarization and modeling of these reactions were performed at Bor Technical faculty. On this occasion, it was established that equivalent electrical circuit must contain very high capacitances, indicating possibility of copper sulfide minerals use as a potential material for electrochemical supercapacitor electrodes [31–33].

2. Experimental

Concerning the preliminary experiments [31–33] which had pointed out the possibility of developing a new type of cupric sulfide-based supercapacitors, a series of experiments on such materials and electrolytes of various compositions has been carried out in order to define an electrochemical system having the best possible features. The standard electrochemical and other methods of material characterization were applied [1,34–37].

2.1. Equipment

The electrochemical characterization was carried out by a standard three-electrode system consisting of saturated calomel electrode (SCE) as a reference electrode, platinum or copper electrode as a counter electrode and a number of working electrodes the active part of which are the tested materials, as shown in Fig. 1. The contact between the copper wire and the electrode material was achieved by using conducting silver glue IM-P3014 (Iritel, Belgrade), and then mounted in SIMGAL mass

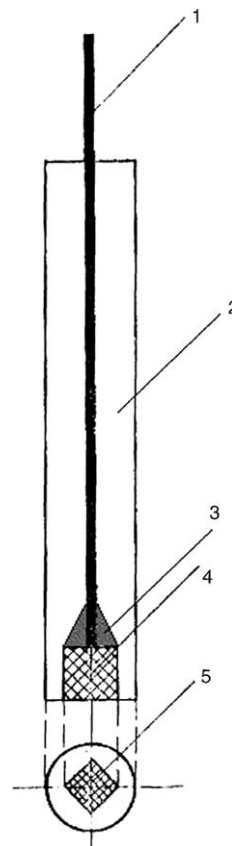


Fig. 1. Construction of working electrode: 1, copper wire; 2, SIMGAL mass; 3, conducting silver glue; 4, electrode material (chalcocite); 5, active surface.

(Galenika, Belgrade). The working electrode was of 27 mm^2 and counter electrode of 200 mm^2 of active surface area.

The system for electrochemical measurements consisted of hardware (PC, AD–DA converter PCI — 20,428 W produced by BURR-BROWN and analog interface developed on Technical faculty in Bor) and software for excitation and measurement (LabVIEW platform and application software).

The optic microscopy of electrode material was carried out by using LOMO MIN9 microscope with digital camera JENOPTIK ProgRes C10+ for the immediate records transfer into the computer. The electronic microscopy was performed by using JSM 35 microscope.

The X-ray analysis was done by Siemens diffractometer Kristalloflex 810.

2.2. Materials

The starting material was samples of natural copper minerals covellite and chalcocite from Bor copper mine and 'white-matte' — the inter-product in copper production, chemically similar to chalcocite. Having performed a series of experiments it was found out that chalcocite showed the best features as a potential electrode material for supercapacitors, subsequently, it was thoroughly explored. Chalcocite is sulfide copper mineral with the highest content of copper, exhibiting high electrical conductivity similar to metals.

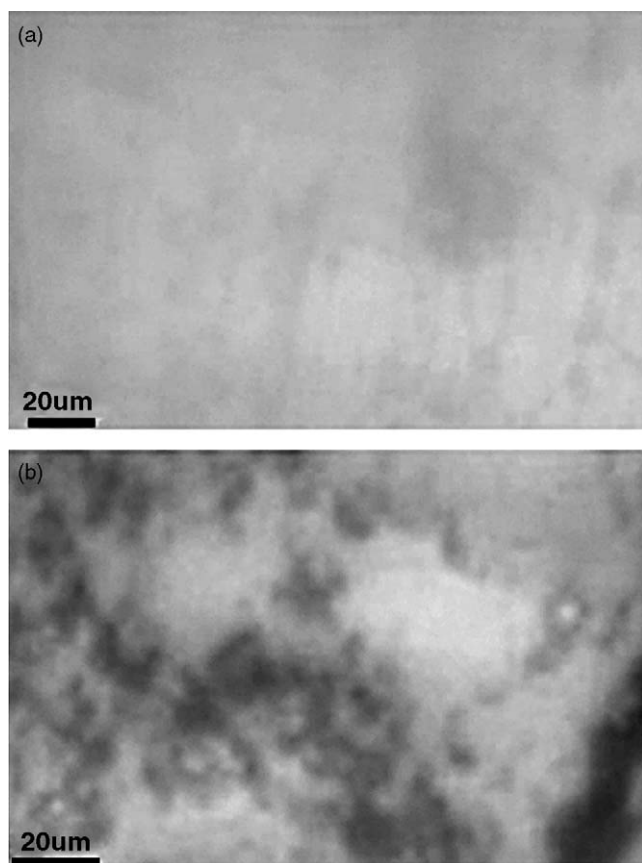


Fig. 2. Microscopic picture of non-treated (a) and treated (b) chalcocite.

The electrode material was examined in various electrolytes but the majority of experiments were done in aqueous solutions of sulfuric acid varying in concentration, with or without the addition of copper sulfate. Merck (sodium carbonate and sodium chloride) and Zorka Šabac (sulfuric acid and copper sulfate) analytical grade reagents were used without further purification.

Solutions were prepared with distilled water and were not de-aerated.

The polished surface of the material was analyzed by optic and electronic microscopy, before and after the application of galvanostatic impulse of 0.5 mA for the duration of 80s in 1 M H_2SO_4 electrolyte.

Fig. 2 shows an optic microscopy picture of the chalcocite sample. Uniform surface of the non-treated sample confirms its high purity concerning natural mineral; natural minerals usually contain some impurities like quartz or pyrite. It is obvious from Fig. 2b that some product appeared on the treated electrode surface during the anodic process. The structure of this product may be considered as the main reason of such high capacitance found out at chalcocite and other copper minerals.

The chemical composition of the material was determined by X-ray diffraction analysis of numerous samples, one of which is presented by the diagram in Fig. 3. The pattern shows that the main constituent of the sample is compound $Cu_{1.097}S$.

2.3. Procedures

For each set of experiments working electrodes were ground, polished, washed out, dried, and finally, submerged into electrolyte fresh made for each series of experiments. Polishing and washing out (without grinding) was done between two experiments. Grinding was performed by the finest grinding paper, polishing by alumina and washing out by distilled water and alcohol.

2.4. All the experiments were performed at room temperature

Having submerged the working electrode, its potential versus the reference electrode was observed, and after stabilization, the value of the rest potential was noted down. The value was used to determine parameters of subsequent experiments depending on the method of examination.

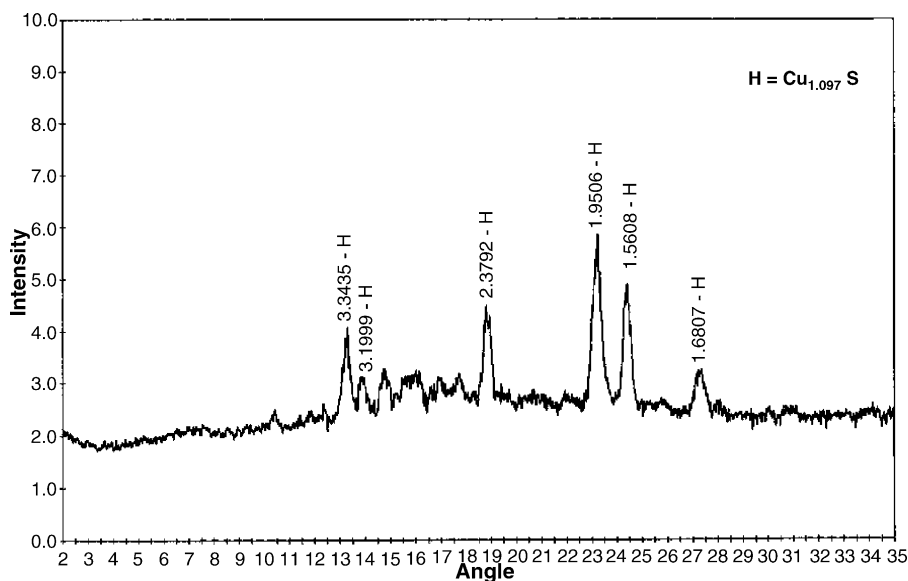
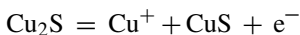


Fig. 3. X-ray diffraction pattern of natural chalcocite.

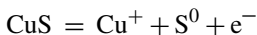
2.5. Possible reaction mechanisms

Oxidation of a sulfide mineral is not a simple, straightforward reaction from the sulfide to the corresponding metal sulfate, but is made up of a series of consecutive reactions.

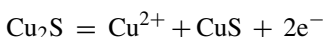
In older literature [38], it can be found a series of assumptions about the mechanism of electrochemical oxidation of chalcocite. Spence and Cook [39], for example, assume next mechanism:



followed by



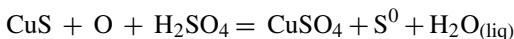
Loshkarev and Vozisov [40] as well as Bulah and Han [41] suppose that the first step in the mechanism of anodic oxidation of chalcocite is reaction:



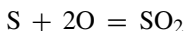
Next step is the discharge of hydroxide ions and oxygen evolution at CuS formed in previous step:



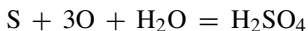
Further dissolution proceeds by chemical oxidation of formed CuS with atomic oxygen produced in previous step:



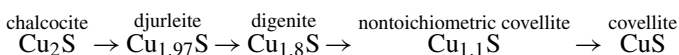
Elemental sulfur also can be oxidized with atomic oxygen, which is very reactive:



or



After Koch [42] anodic dissolution of chalcocite proceeds through a series of intermediary reactions:



Further oxidation of covellite is slow and results in formation of elemental sulfur.

Brennet et al. [43] confirmed that mechanism, but they could not prove the presence of djurleite.

The last assumption seems to be nearest to the real mechanism. It can be assumed that the metal ions from the mineral crystal lattice are transferred into the solution leaving a surface region with the higher content of sulfur. That sulfur can be treated as adsorbed species giving rise to the pseudocapacitance exhibited by Cu₂S.

3. Results and discussion

3.1. Galvanostatic examination

Classic galvanostatic method assumes that the system is excited by the constant current between working and counter electrode in a determined time interval. The overvoltage related to reference electrode is denoted as the system response. Besides

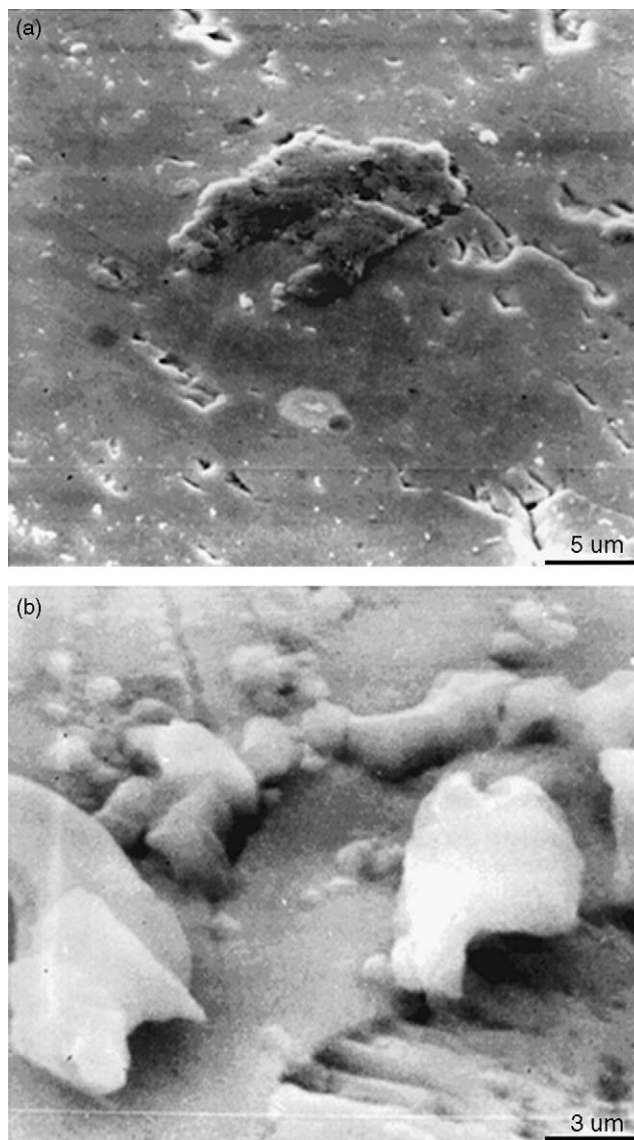


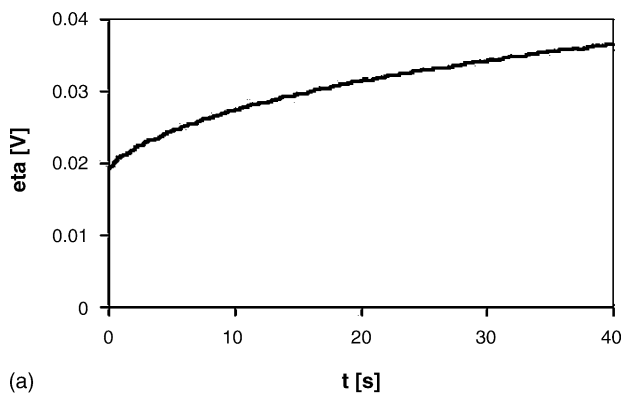
Fig. 4. Electronic microscopy picture of (a) non-treated chalcocite and (b) treated chalcocite.

the classical, the modified method [31,33] with prolonged duration of current impulse is applied in order to allow the overwhelming system analysis. The surface of the electrode is also analyzed before and after the use of galvanostatic impulse.

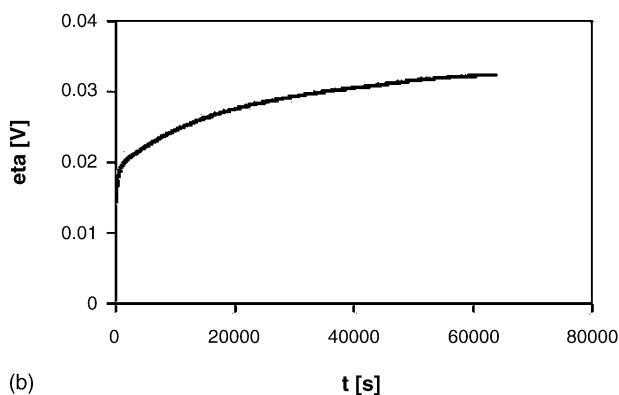
Fig. 4 shows an electronic microscopy picture of the chalcocite sample before and after the application of galvanostatic impulse of 0.5 mA for the duration of 80 s in 1 M H₂SO₄ electrolyte. The consequences of the reaction on the treated samples are obvious so as their non-homogeneous surface layer, noticeably porous, hence the increase of the electrode interface.

A series of experiments on chalcocite electrodes in the 0.5 M H₂SO₄ + 1 M NaCl electrolyte showed the intense self-discharge effect (electrodes tend to relax quickly), so the project was abandoned.

All the prepared electrodes were examined in the unimolar solution of pure sulfuric acid (1 M H₂SO₄), but it resulted in excessive serial resistance of the system.



(a)



(b)

Fig. 5. Galvanostatic curve of chalcocite in 1 M H_2SO_4 + 0.1 M CuSO_4 aqueous solution: excitation (a) 3 mA, 40 s; (b) 0.1 mA, 63,000 s.

Galvanostatic curve for the chalcocite electrode subjected to excitation of 3 mA for the duration of 40 s in the solution of sulfuric acid and copper sulfate is given in Fig. 5a, and subjected to excitation of 0.1 mA for the duration of 63,000 s in Fig. 5b.

Parameters of the electrochemical system such as serial resistance, leakage current and the capacitance as the main parameter for further investigations, have been determined from experimentally obtained diagrams. From the diagrams presented in Fig. 5, it was obtained a capacitance of 26.8 F for chalcocite in 1 M H_2SO_4 + 0.1 M CuSO_4 electrolyte. When operating voltage is 0.6 V, leakage current has a quite large value of 1.9 mA and there is the need for further optimization of the system from that particular point of view.

Henceforward, the overvoltage was measured on the same working electrode in the electrolyte 1 M H_2SO_4 + 0.1 M CuSO_4 related to the reference and the counter electrode (Fig. 6).

It was noticed that the copper electrode shows great stability and that the increase of overvoltage between the working and the counter electrodes is small related to the overvoltage between the working and the reference electrode, which, apart from economic reasons, resulted in adoption of copper counter electrode.

3.2. Cyclic voltammetry

Since the time constants of examined electrochemical systems were high, the standard cyclic voltammetry method at a low sweep rate was applied.

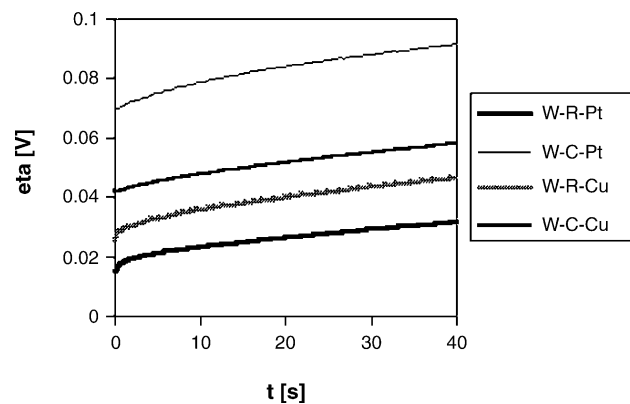


Fig. 6. Diagram of overvoltage between working and reference electrodes (W–R), and between working and counter electrodes (W–C), where the counter electrode is made of platinum (Pt) or copper (Cu).

A series of experiments was carried out on various electrochemical systems with varying sweep rate in order to determine the optimum working conditions.

Fig. 7 shows voltammetric curve of chalcocite electrode in 1 M H_2SO_4 + 0.1 M CuSO_4 obtained using a sweep rate of $10 \mu\text{V s}^{-1}$. The shape of the curve, nearly the same absolute values of positive and negative maximum currents and the surface area confined with the voltammogram, which is proportional to capacitance of the system point out at capacitive behavior of the system. The lack of vertical part of the curve is the result of higher serial resistance and partial irreversibility of the processes occurring at the electrode.

The surface area of the loop was measured yielding the determination of capacitance of $C_2 = 32.2 \text{ F}$.

3.3. Potentiostatic research

The advantage of potentiostatic method – relatively short duration of the experiment – was made use of for the detailed investigation of the electrode material behavior in various electrolytes for the purpose of optimum electrolyte distinction con-

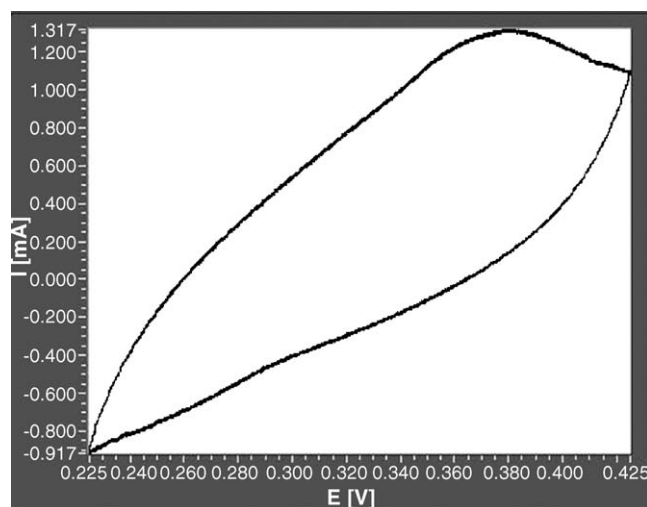


Fig. 7. Voltammetric curve of chalcocite in 1 M H_2SO_4 + 0.1 M CuSO_4 at $dE/dt = 10 \mu\text{V s}^{-1}$.

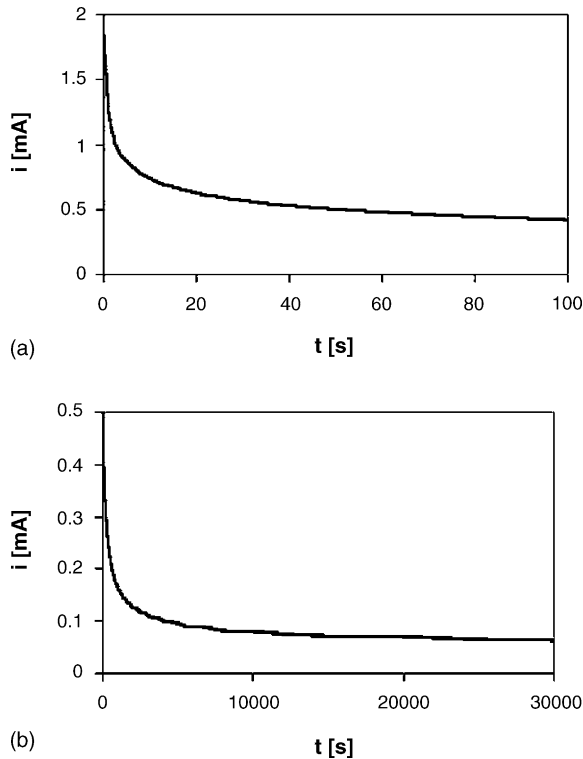


Fig. 8. Potentiostatic curves of chalcocite electrode in the solution of 1 M H_2SO_4 + 0.1 M CuSO_4 for (a) shorter period (b) longer period.

cerning the obtention of maximum capacitance and minimum leakage current.

Fig. 8 shows the potentiostatic curve ($\eta = 20$ mV) for chalcocite electrode in 1 M solution of sulfuric acid with the addition of 0.1 M of copper sulfate. Fig. 9 shows the family of potentiostatic curves with the concentration of CuSO_4 as a parameter.

It was determined that capacitance C_2 increases with the concentration of CuSO_4 , having the increase of self-discharge as a side phenomenon, so the optimum concentration was estimated to be 0.1 M CuSO_4 .

3.4. Electrochemical impedance spectroscopy (EIS)

Since EIS, if applied on the systems containing high capacitances, demands long duration of experiments [37], just few

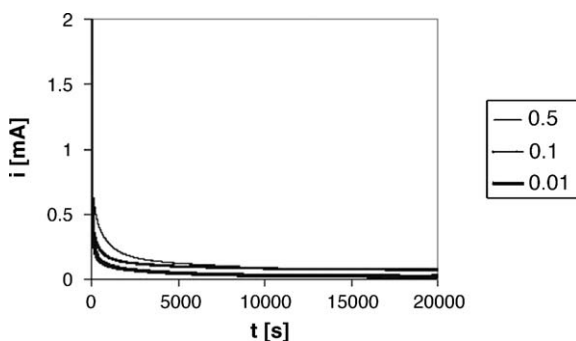


Fig. 9. Family of potentiostatic curves for various concentrations of copper sulfate.

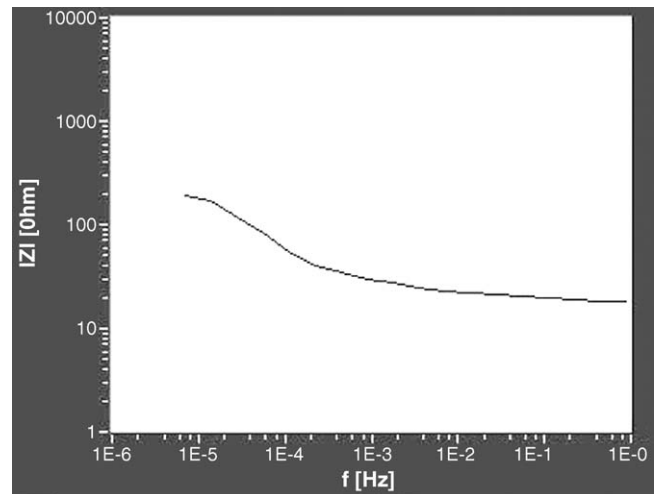


Fig. 10. Impedance diagram for chalcocite electrode in 1 M H_2SO_4 + 0.1 M CuSO_4 .

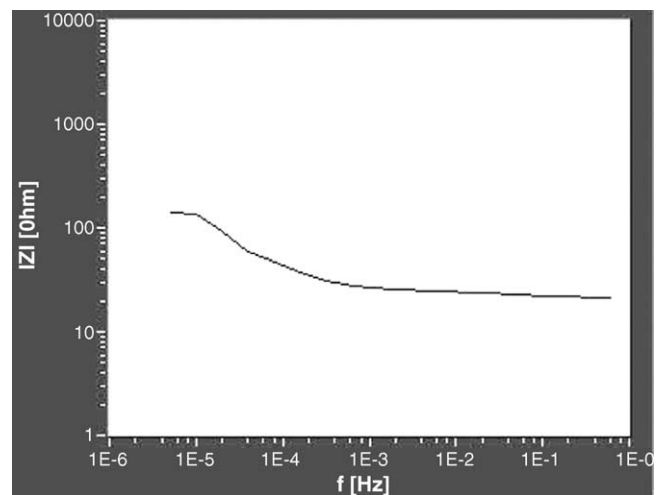


Fig. 11. Impedance diagram for chalcocite electrode in 1 M H_2SO_4 + 0.5 M CuSO_4 .

characteristic electrochemical systems were examined by this method.

Fig. 10 shows the impedance diagram of chalcocite electrode in the solution of 1 M H_2SO_4 + 0.1 M CuSO_4 . Fig. 11 stands for the same system with 0.5 M CuSO_4 added.

The excitation voltages were $V_{\text{DC}} = 20$ mV, $V_{\text{AC max}} = 5$ mV.

From the diagrams presented in Figs. 10 and 11 it was obtained a capacitance of 29.9 F for chalcocite in 1 M H_2SO_4 + 0.1 M CuSO_4 (leakage current at 0.6 V is 3.2 mA) and 65.8 F in 1 M H_2SO_4 + 0.5 M CuSO_4 (leakage current at 0.6 V is 4.2 mA). The last value is the highest obtained at investigated systems, but leakage current is the highest, too.

4. Conclusion

A number of chalcocite electrodes were examined in various electrolytes and the preliminary optimization of the system was performed from the aspect of its application for electrochemical supercapacitors considering two key parameters — capacitance

and leakage current. Further optimization is needed in order to decrease serial resistance and improve other parameters. All the methods applied pointed out at high value of capacitance (approximately 110 and 200 F cm⁻², depending on electrolyte) which implies that chalcocite is likely to be a new material for supercapacitors.

References

- [1] B.E. Conway, *Electrochemical Supercapacitors*, Kluwer Academic Publishers, New York, 1999.
- [2] R. Kotz, M. Carlen, *Electrochim. Acta* 45 (2000) 2483.
- [3] C. Arbizzani, M. Mastragostino, F. Soavi, *J. Power Sources* 100 (2001) 164–170.
- [4] B.E. Conway, W.G. Pell, *J. Power Sources* 105 (2002) 169–181.
- [5] G.L. Paul, A.M. Vassalo, *Proceedings on Power Pulse*, New York, 2000, p. 101.
- [6] R. Kotz, M. Carlen, *Electrochim. Acta* 45 (2000) 2483.
- [7] J.P. Zheng, J. Huang, T.R. Jow, *J. Electrochem. Soc.* 144 (6) (1997) 2026.
- [8] D. Qu, *Studies, J. Power Sources* 109 (2002) 403–410.
- [9] E. Frackowiak, F. Beguin, *Carbon* 39 (6) (2001) 937–950.
- [10] L. Bonnefoi, P. Simon, J.F. Fauvarque, C. Sarrazin, A. Dugast, *J. Power Sources* 79 (1) (1999) 37–42.
- [11] H.B. Gu, J.U. Kim, H.W. Song, G.C. Park, B.K. Park, *Electrochim. Acta* 45 (2000) 1533–1536.
- [12] K.H. An, K.K. Jeon, W.S. Kim, Y.S. Park, S.C. Lim, D.J. Bae, J.H. Lee, *J. Korean Phys. Soc.* 39 (2001) S511–S517.
- [13] M. Wohlfahrt-Mehrens, J. Schenk, P.M. Wilde, E. Abdelmula, P. Axmann, J. Garche, *J. Power Sources* 105 (2002) 182–188.
- [14] K. Okajima, A. Ikeda, K. Kamashita, M. Sudoh, *Electrochim. Acta* 51 (2005) 972–977.
- [15] A. Celzard, F. Collas, J.F. Mareche, G. Furdin, I. Rey, *J. Power Sources* 108 (2002) 153–162.
- [16] R.N. Reddy, R.G. Reddy, *J. Power Sources* 124 (1) (2003) 330–337.
- [17] Y.U. Jeong, A. Manthiram, *J. Electrochem. Soc.* 148 (3) (2001) A189–A193.
- [18] J.P. Zheng, P.J. Cygan, T.R. Jow, *J. Electrochem. Soc.* 142 (1995) 2699.
- [19] J.M. Miller, B. Dunn, T.D. Tran, R.W. Pekala, *J. Electrochem. Soc.* 144 (1997).
- [20] M. Ramani, B.S. Haran, R.E. White, B.N. Popov, Lj. Arsov, *J. Power Sources* 93 (2001) 209–214.
- [21] E. Frackowiak, F. Beguin, *Carbon* 40 (10) (2002) 1775–1787.
- [22] E. Frackowiak, K. Jurewicz, F. Beguin, K. Szastak, S. Delpoux, *Process. Technol.* 77–78 (1–3) (2002) 213–219.
- [23] P.V. Adhyapak, T. Maddanimath, S. Pethkar, A.J. Chandwadkar, J.S. Negi, K. Vijayamohanan, *J. Power Sources* 109 (2002) 105–110.
- [24] J.M. Miller, B. Dunn, *J. Electrochem. Soc.* 144 (12) (1997) L309–L311.
- [25] C. Emmenegger, P. Mauron, P. Sudan, P. Wenger, V. Hermann, R. Gallay, A. Zuttel, *J. Power Sources* 124 (2003) 321–329.
- [26] J.H. Park, J.M. Ko, O.O. Park, *J. Electrochem. Soc.* 150 (7) (2003) A864–A867.
- [27] Chan Kim, *J. Power Sources* 142 (2005) 382–388.
- [28] P. Velasquez, D. Leinen, J. Pascual, J.R. Ramos-Barrado, R. Cordova, H. Gomez, R. Schrebler, *J. Electroanal. Chem.* 501 (2001) 20–28.
- [29] D.F.A. Koch, *Electrochemistry of sulfide minerals*, in: J.O'M. Bockris, B.E. Conway (Eds.), *Modern Aspects of Electrochemistry*, vol. 10, Plenum Press, New York, 1975 (Chapter 4).
- [30] D. Tsamouras, L. Kobotiatas, E. Dalas, S. Sakkopoulos, *J. Electroanal. Chem.* 469 (1) (1999) 43–47.
- [31] M. Rajčić-Vujasinović, Z. Stanković, Z. Stević, *Elektrokhimiya* 35 (3) (1999) 347–354.
- [32] Z. Stević, M. Rajčić-Vujasinović, Z. Stanković, *Proceedings of the 34th International October Conference on Mining and Metallurgy, Bor Lake, October 2002, 2002*, pp. 435–440.
- [33] Z. Stević, M. Rajčić-Vujasinović, Z. Stanković, *Proceedings of the 3rd International Conference of the Chemical Societies of the South-Eastern European Countries on Chemistry in the New Millennium — An Endless Frontier, Bucharest, Romania, September 2002, Book of Abstracts, vol. II, 2002*, p. 97.
- [34] W.G. Pell, B.E. Conway, *J. Electroanal. Chem.* 500 (1–2) (2001) 121–133.
- [35] C. Arbizzani, M. Mastragostino, L. Meneghello, *Electrochim. Acta* 40 (13–14) (1995) 2223–2228.
- [36] P. Kurzweil, H.-J. Fischle, *J. Power Sources* 127 (2004) 331–340.
- [37] Z. Stević, *Supercapacitors based on copper sulfides*, Ph.D. Thesis, Belgrade, 2004.
- [38] M. Sato, *Econom. Geol.* 55 (1960) 1202–1231.
- [39] W.W. Spence, V.R. Cook, *Transactions LXVII* (1964) 257–263.
- [40] A.G. Loshkarev, A.F. Vozisov, *Zh. Prikl. Khim* XXVI (1) (1953) 55–60.
- [41] A.A. Bulah, O.A. Han, *Zh. Pzikh. Khim.* XXVII (2) (1954) 166–170.
- [42] D.F.A. Koch, in: J.O'M. Bockris, B.E. Conway (Eds.), *Modern Aspects of Electrochemistry*, vol. 10, Plenum Press, New York, 1975 (Chapter 4).
- [43] P. Brennet, S. Jaffareli, J.M. Vansevern, J. Verecken, R. Winnand, *Metall. Trans.* 5 (1974) 127.